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On the Determination of Absolute Intensities from Single- and Multiple-Path Absorption Measurements*

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The physical principles involved in conventional absolute intensity measurements are reviewed. Experimental difficulties rule out the use of extrapolation techniques for some spectral transitions. For this reason it is of interest to re-examine the possibility of using total absorption measurements, in conjunction with the curves of growth, for making intensity estimates. Extrapolation methods yield results which are independent of spectral line shape. Use of the curves of growth, on the other hand, implies the assumption that the line contour can be described by combined Doppler and Lorentz broadening.

The curves of growth permit a unique correlation between total absorption and f-value either for spectral lines with pure Doppler broadening or for pure collision broadening. Furthermore, a simple experimental procedure can be devised for estimating both the absolute intensity and the spectral line profile on the basis of single-path and multiple-path absorption measurements. The suggested procedure involves absorption measurements for optical densities (path lengths) under conditions in which the integrated fractional absorption is a relatively sensitive function of spectral line shape. Representative calculations referring to utilization of the proposed method have been carried out for spectral lines belonging to the $^2\Sigma \rightarrow {}^2\Pi$ transitions, (0,0)-band, of OH, and also for lines belonging to the fundamental vibration-rotation spectrum of CO.

I. INTRODUCTION

THE difficulties inherent in quantitative measurements of intensities are well-known to spectroscopists.

For absolute intensity estimates on isolated spectral lines in ultraviolet spectra probably the most widely used procedure involves measurement of the integrated fractional absorption, followed by attempts at estimating f-values through the use of the curves of growth.[1] If accurate measurements can be made for sufficiently small optical densities, unambiguous interpretation of the results is possible since the fractional absorption is independent of spectral line-shape.[2] Less satisfactory is the type of interpretation used, for example, in the determination of absolute f-values for lines belonging to $^2\Sigma \rightarrow {}^2\Pi$ transitions of OH.[3,4] In this case the integrated fractional absorption depends upon both line shape and absolute intensity. Consequently, fitting of observed data to theoretical curves for relative intensities involves such doubtful assumptions as uniform line shape for all of the measured lines, relative intensity estimates which neglect vibration-rotation interactions, etc. It is evident that a more satisfactory approach for conditions corresponding to nonlinear portions of the curves of growth must involve two independent measurements for each spectral line in order to determine the two unknowns involved, *viz.*, line shape and f-value. This suggested procedure is applicable to all spectral lines which are adequately described by combined Doppler and Lorentz broadening, irrespective of the spectral region in which the lines under study occur.

Reliable infrared intensity measurements for entire vibration-rotation bands can be carried out by judicious use of extrapolation techniques[5] combined with suitable methods for pressure broadening.[6] Since the experimental conditions required for intensity estimates are sometimes difficult to meet, particularly for diatomic molecules, use of the procedure based on the curves of growth is indicated in some cases.

There are two basic assumptions involved in the use of the curves of growth for line shape and intensity estimates. These are: (1) the spectral lines under study have a contour which is described adequately by a representation based on Lorentz and Doppler broadening; (2) the measured integrated fractional absorption is substantially independent of experimental slit width. There is experimental evidence that the first assumption is often a useful empirical rule in the sense that observed experimental data can be made to fit a simplified spectral line contour, although the actual line shape may not correspond exactly to the Doppler-Lorentz broadening formula.[7] It is easily shown[8,9] that

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[1] E. M. F. van der Held, Z. Physik **70**, 508 (1931); S. S. Penner and R. W. Kavanagh, J. Opt. Soc. Am. **43**, 385 (1953).

[2] R. B. King and D. C. Stockbarger, Astrophys. J. **91**, 488 (1940); **95**, 78 (1942).

[3] O. Oldenberg and F. F. Rieke, J. Chem. Phys. **6**, 439 (1938); R. J. Dwyer and O. Oldenberg, *ibid.* **12**, 351 (1944).

[4] P. J. Dyne, Technical Report No. 12, Contract Nonr-220(03), NR 015 210, California Institute of Technology, Pasadena, November, 1953.

[5] E. B. Wilson, Jr., and A. J. Wells, J. Chem. Phys. **14**, 578 (1946).

[6] S. S. Penner and D. Weber, J. Chem. Phys. **19**, 807, 817, 974 (1951).

[7] For discussions of spectral line shape see, for example, H. Margenau and W. W. Watson, Revs. Modern Phys. **8**, 22 (1936); J. H. Van Vleck and V. F. Weisskopf, *ibid.* **17**, 227 (1945); P. W. Anderson, Phys. Rev. **76**, 647 (1949).

[8] Nielsen, Thornton, and Dale, Revs. Modern Phys. **16**, 307 (1944).

[9] C. R. De Prima and S. S. Penner, J. Chem. Phys. **23**, 775 (1955).

the second statement is correct, in principle; errors resulting from lack of experimental sensitivity will be discussed in a subsequent publication.

In Sec. II we present a brief review of the physical principles involved in the use of extrapolation techniques for absolute intensity measurements. Absolute intensity and line-shape estimates through the curves of growth are considered in Sec. III. Application of the proposed procedure to $^2\Sigma \rightarrow {}^2\Pi$ transitions of OH, (0,0)-band, is described in Sec. IV. Representative calculations for spectral lines belonging to the fundamental vibration-rotation band of CO are given in Sec. V.

II. EXTRAPOLATION TECHNIQUES FOR ABSOLUTE INTENSITY MEASUREMENTS

The fractional absorption, $A(\omega)$, and the fractional transmission, $T(\omega)$, are related through the expression

$$A(\omega)=1-T(\omega). \tag{1}$$

If $P(\omega)$ is the spectral absorption coefficient at the wave number ω and X equals the optical density, then

$$\int_{\omega_1}^{\omega_2} A(\omega)d\omega=\int_{\omega_1}^{\omega_2}\{1-\exp[-P(\omega)X]\}d\omega \tag{2}$$

independently of the experimental slit function, provided the integration interval from ω_1 to ω_2 exceeds the wave-number range, for which $P(\omega)$ vanishes, by the experimental slit width $\Delta\omega^*$ on either side.[9,10] It should be noted also that the validity of Eq. (2) does not depend on the functional form of $P(\omega)$ provided $P(\omega)$ vanishes for $\omega \leq \omega_1+\Delta\omega^*$ and for $\omega_2-\Delta\omega^* \leq \omega$. From Eq. (2) is is apparent that

$$S_K=\int_{\omega_1}^{\omega_2} P(\omega)d\omega=\lim_{X\rightarrow 0}\left[(1/X)\int_{\omega_1}^{\omega_2} A(\omega)d\omega\right] \tag{3}$$

where S_K represents the integrated intensity of the spectral line under study whose center is assumed to lie at the wave number ω_K. The validity of Eq. (3) for all slit functions and line shapes forms the basis of extrapolation methods for the determination of absolute intensities.[5,6,11,12] Extrapolation methods will fail to yield reliable results only if $\int_{\omega_1}^{\omega_2} A(\omega)d\omega$ is not estimated correctly at very low optical densities because of lack of intrumental sensitivity. In this case the limiting curvature of a plot of $\int_{\omega_1}^{\omega_2} A(\omega)d\omega$ *vs* X is not defined properly, and extrapolation to $X=0$ leads to an erroneous estimate for S_K.

Significant absolute intensity estimates are obtained also if the experimental slit width is small compared to the line width.[6] Under these conditions $P(\omega)$ is measured directly and

$$S_K=\int_{\omega_1}^{\omega_2} P(\omega)d\omega=-\frac{1}{X}\int_{\omega_1}^{\omega_2}[\ln T(\omega)]d\omega \tag{4}$$

defines the integrated intensity. Experimental conditions justifying the use of Eq. (4) can be approached at elevated pressures. In practice a combination of pressure broadening and extrapolation to zero optical pathlength leads to the most desirable results.[6]

It is apparent from the preceding considerations that there is a need for methods of obtaining reliable intensity estimates under conditions where pressure broadening and/or extrapolation to zero optical pathlength is not feasible. For this reason we propose to re-examine the use of the curves of growth for the interpretation of integrated fractional absorption measurements, particularly under conditions in which the measured results are a sensitive function of the line-shape parameter.

III. USE OF THE CURVES OF GROWTH FOR ABSOLUTE INTENSITY AND LINE-SHAPE MEASUREMENTS

The integrated fractional absorption is again determined through Eq. (2) while the integrated intensity S_K is defined in Eq. (4). If the spectral line under study had a pure Doppler contour the (maximum) absorption coefficient at the line center would be

$$P_K'=(S_K/\omega_K)(mc^2/2\pi kT)^{\frac{1}{2}} \tag{5}$$

where m is the mass of the radiating molecule, c equals the velocity of light, k equals the Boltzmann constant, and T is the absolute temperature. A spectral line with combined Doppler, collision, and natural line broadening is described conveniently by the parameter

$$a=(b_N+b_C)(\ln 2)^{\frac{1}{2}}/b_D, \tag{6}$$

where b_N, b_C, and b_D denote, respectively, the natural half-width, the half-width resulting from collision (Lorentz) broadening, and the half-width produced by Doppler broadening.[13]

The spectral absorption coefficient $P(\omega)$ entering into Eq. (2) is a linear function of P_K' and depends also on the line-shape parameter a. In the conventional curves of growth $A(\ln 2)^{\frac{1}{2}}/2b_D$ is plotted as a function of $P_K'X$ with a treated as a variable parameter,[1] where

$$(\ln 2)^{\frac{1}{2}}/b_D=(1/\omega_K)(mc^2/2kT)^{\frac{1}{2}}.$$

Let A_1 and A_2 represent, respectively, the total fractional absorption for the K'th spectral line if the optical pathlengths have the values X_1 and X_2, respectively. It is then a simple matter to obtain A_1 and A_2 as functions of $P_K'X_1$ and a for known values of X_2/X_1 through use of the curves of growth. Alternately, the ratio A_2/A_1 can be represented as a function of $P_K'X_1$

[10] The experimental slit width $\Delta\omega^*$ is defined by the condition that the slit function $g(|\omega'-\omega|,b,c)$ vanishes for $|\omega'-\omega| \geq \Delta\omega^*$ where $g(|\omega'-\omega|,b,c)$ determines the contributions to the measured intensity, when the instrument is set at the wave number ω, resulting from the wave number ω'.

[11] D. G. Bourgin, Phys. Rev. **29**, 794 (1927); **32**, 237 (1928).

[12] Thorndike, Wells, and Wilson, J. Chem. Phys. **15**, 157 (1947).

[13] The half-width is defined as the wave-number range for which $P(\omega)$ is greater than or equal to one-half of the spectral absorption coefficient at the line center.

and a, as has been done in a previous publication for the special case $X_2/X_1=2$.[14]

From the measured values of A_1 and A_2 and the known ratio X_2/X_1 we can construct two curves relating a to $P_K'X_1$. The applicable values of a and $P_K'X_1$ for the absorbing system correspond to the intersection of the two curves of a *vs* $P_K'X_1$. Finally, since X_1 is known from the partial pressure of absorbing gas and from the length of the gas absorption cell, P_K' itself is determined. The integrated intensity S_K may now be calculated from Eq. (5). Alternately, the dimensionless oscillator strength f_K associated with the K'th line is given through the expression

$$S_K=2.379\times10^7(273.1/T)f_K(N_l/N_T)\times[1-\exp(-hc\omega_K/kT)] \quad (7)$$

where N_l/N_T represents the fraction of the total number of absorbing molecules in the lower state for the transition or transitions giving rise to the line with quantum number K, and h is Planck's constant.

If experimental measurements are made for a series of spectral lines belonging to a given electronic transition or vibration-rotation band, and if the relative intensities can be calculated theoretically, a simple experimental check is available for the consistency of the data as well as for the correctness of the relative intensity calculations. Thus

$$S_K=\frac{8\pi^3N_T}{3hcQ}\omega_K g_u(q_K)^2[\exp(-E_l/kT)]\times[1-\exp(-hc\omega_K/kT)] \quad (8)$$

where Q is the total partition function, g_u equals the statistical weight of the upper state involved in the transition giving rise to the K'th spectral line, $(q_K)^2$ is the square of the matrix element for the transition under study, and E_l is the lower energy level of the absorbing (ground) state. From Eqs. (5) and (8) it is easily shown[15] that

$$P_K'\frac{3hcQ}{8\pi^3N_T}\left(\frac{2\pi kT}{mc^2}\right)^{\frac{1}{2}}[\exp(E_l/kT)][g_u(q_K)^2]^{-1}=1. \quad (9)$$

A plot of the left-hand side of Eq. (9) as a function of K would be expected to show systematic deviations from unity if, for example, significant vibration-rotation interactions had been neglected in the calculation of $g_u(q_K)^2$. Alternately, if correct theoretical values are available for $g_u(q_K)^2$, then consistency of the experimental data can be verified by showing that $\ln[S_K/g_u(q_K)^2]$ is a linear function of E_l with slope equal to $-1/kT$.

[14] S. S. Penner, J. Chem. Phys. **21**, 686 (1953).

[15] The factor $[1-\exp(-hc\omega_K/kT)]$ is practically equal to unity at all reasonable temperatures for absorption experiments in the visible and infrared regions of the spectrum.

IV. INTENSITY ESTIMATES ON SPECTRAL LINES BELONGING TO $^2\Sigma\rightarrow{}^2\Pi$ TRANSITIONS OF OH, (0,0)-BAND

We proceed to examine the required experimental conditions for an accurate redetermination of f-values for spectral lines belonging to $^2\Sigma\rightarrow{}^2\Pi$ transitions, (0,0)-band, of OH, using in our calculations for the determination of suitable experimental conditions the absolute intensity estimates of Oldenberg and Rieke[3]; the argument remains substantially unchanged if Dyne's f-values are employed.

Consider an absorption experiment in a 50-cm long cell on the OH formed in a mixture consisting initially of two parts of H_2O and one part of O_2 at atmospheric pressure. Equilibrium calculations at 1300°K show that $X=1.185\times10^{-3}$ cm-atmos.[16] According to Oldenberg and Rieke[3,4] the f-value for the $Q_1(K=6)$ line is

$$f=3.17\times10^{-4}S_J/(2J+1) \quad (10)$$

where the rotational line strength $S_J=50.6$ if vibration-rotation interactions are neglected,[17] and $2J+1$ (with $J=K+\frac{1}{2}$) is the statistical weight of the lower energy level involved in the given transition.

The use of Eqs. (5), (7), and (10) and introduction of appropriate numerical values shows that $P_K'=1.64\times10^3$ $\text{cm}^{-1}-\text{atmos}^{-1}$ for the $Q_1(6)$ line. Hence $\log(10.6P_K'X)\simeq1.30$ would represent the abscissa of the curves of growth. This numerical value, together with the line-shape parameter a determines A_1. For the sake of argument we assume $a=1$. A triple-path experiment for the same value of a and $\log(10.6P_K'X)$ increased by log 3 corresponds to the value of A_2. In practice A_1 and A_2 are determined with a and $P_K'X$ unknown. In Fig. 1 we show a plot of the possible values of a as a function of $P_K'X$ for a measured value of $A_1(\ln2)^{\frac{1}{2}}/2b_D=1.35$; this curve is seen to intersect the a *vs* $P_K'X$ curve corresponding to the value $A_2(\ln2)^{\frac{1}{2}}/2b_D=3.00$ for a triple-path experiment at $a=1$ and $\log(10.6P_K'X)=1.30$. Reference to Fig. 1 shows that both a and $P_K'X$ can be determined with acceptable accuracy as long as the true values are roughly the same as those assumed in the present illustrative calculations. In other words, the use of single- and triple-path absorption measurements on OH in a 50 cm long tube at 1300°K appears to be a promising experiment for a redetermination of the f-value, provided (1) the spectral line shape is described by combined Doppler and Lorentz broadening, and (2) adequate experimental sensitivity is obtained.

A single measurement of integrated fractional absorption would determine $P_K'X$ if a is either very nearly zero or else very large (say $a>10$). Alternately, if

[16] This result is based on the thermodynamic functions prepared by the National Bureau of Standards and listed in "Tables of Selected Values of Chemical Thermodynamic Properties," Series I, Volume I, 1947-1949.

[17] G. H. Dieke and H. M. Crosswhite, Bumblebee Series Report No. 87, The Johns Hopkins University, Baltimore, November, 1948.

sufficient experimental sensitivity can be obtained to determine the integrated fractional absorption for $\log(10.6P_K'X)$ less than about 0.5, then $P_K'X$ is roughly determined independently of the absolute value of a.

V. INTENSITY ESTIMATES ON SPECTRAL LINES BELONGING TO THE FUNDAMENTAL VIBRATION-ROTATION BAND OF CO

The nonlinear parts of the curves of growth may also be used, in principle, to determine infrared intensities and the line-shape parameter a for lines with Doppler and Lorentz broadening. A graph similar to the one shown in Fig. 1 applies under suitable experimental conditions.

For CO at 300°K the integrated intensity for the rotational line $J=6\rightarrow J=7$ belonging to the fundamental vibration-rotation band ($n=0\rightarrow n=1$) is found to have the value $S_{6\rightarrow 7}{}^{0\rightarrow 1}=9.98$ cm^{-2}-atmos^{-1}.[6,18,19] The center of this spectral line occurs at 2169 cm^{-1}.

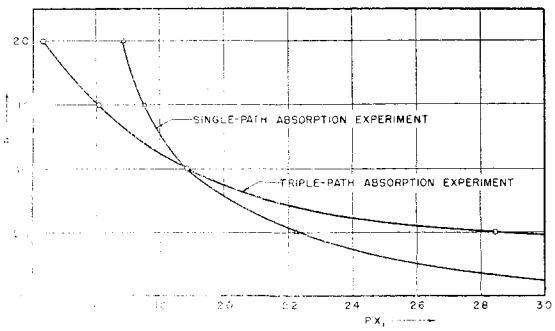

FIG. 1. Illustrative plot indicating the interpretation of single-path and triple-path absorption experiments for $a=1$ and $P'X_1=1.88$.

Therefore $P_K'=1.85\times 10^3$ cm^{-1}-atmos^{-1}. For $X_1=10^{-3}$ cm-atmos, $\log(10.6P'X)\simeq 1.3$ and, if $a\simeq 1$, Fig. 1 applies again for $X_2=3\times 10^{-3}$ cm-atmos. If the collision half-width for CO at 300°K and atmospheric pressure[20] is 0.065 cm^{-1}, then $a\simeq 1$ at a total pressure of about 0.05 atmos. It is of interest to note that $a\simeq 20$ at atmospheric pressure and room temperature for CO.

[18] "Wave Number and Intensity Tables for Carbon Monoxide," Contract Nonr-220(03), NR 015 210, California Institute of Technology, Pasadena, September 1952.

[19] J. R. Oppenheimer, Proc. Cambridge Phil. Soc. **23**, 327 (1926); R. C. Herman and R. F. Wallis, J. Chem. Phys. **23**, 637 (1955).

[20] S. S. Penner and D. Weber, J. Chem. Phys. **19**, 1361 (1951); **21**, 1503 (1953).